A Pilot Plant for Removing Chromium from Residual Water of Tanneries

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The purpose of this study is to develop a technical process for removing trivalent chromium from tannery wastewater via precipitation. This process can be considered an alternative that avoids a remediation procedure against the metal presence in industrial wastes. This process was verified in a treatment pilot plant located in León, México handling 10 m^3/day of three types of effluents. The effluent streams were separated to facilitate the elimination of pollutants from each one. The process was based on *in situ* treatment and recycle to reduce problems associated with transportation and confinement of contaminated sludges. Two types of treatment were carried out in the pilot plant: The physical/chemical and biological treatments. Thirty-five experiments were conducted and the studied variables were the pH, type of flocculant, and its dose. The statistical significance of chromium samples was 94.7% for its precipitation and 99.7% for recovery. The objectives established for this phase of the development were accomplished and the overall efficiencies were measured for each stage in the pilot plant. The results were: *a*) chromium precipitation 99.5% from wastewater stream, *b*) chromium recovery 99% for recycling, and *c*) physical/chemical treatment to eliminate grease and fat at least 85% and 65 to 70% for the biological treatment. The tanning of a hide lot (350 pieces) was accomplished using 60% treated and recycled water without affecting the product quality. The recovered chromium liquor was also used in this hide tanning. This technical procedure is also applicable for removing heavy metals in other industrial sectors as well as in reducing water consumption rates, if pertinent adjustments are implemented. — Environ Health Perspect 103(Suppl 1):63–65 (1995)

Key words: chromium, pilot plant, precipitation, process, remediation, tanneries, technology, treatment, wastewater

Introduction

The manufacturing processes for leather tanning require considerable quantities of wastewater to be discharged to the sewer and irrigation channels. This wastewater contains two types of noxious pollutants with potential impact on the health of aquatic life and recreation (*1*): toxic compounds such as Cr(III) and S(–II), and conventional pollutants and indicators, such as biological oxygen demand, chemical oxygen demand, grease, total suspended solids, pH, Cl, and total dissolved solids. Technologies that are available to treat tanning waste (*2,3*) were developed for various operating conditions and are not directly applicable in geographic regions with a limited water supply.

On the other hand, regulatory standards to control pollutant discharges are now enforced in a strict manner for most industrial sectors. Likewise, the production and wastewater treatment costs of tanneries must be minimized to increase profitability.

Consequently, the purpose of this research was to develop a treatment process for the effluents generated in the tanneries of León, Gto., México, with the following goals:

- treated water must fulfill ecological regulations;
- a large portion of treated water must be recycled to the tanning process without affecting the quality of the hides;
- chromium removed from the effluent must be reused in the tanning process to avoid landfilling, confinement, or bioremediation;
- treatment must be economically feasible (*4*).

Materials and Methods

The treatment process for removing chromium and other substances was developed in accordance with physical/chemical principles (*5*), engineering criteria (*6*), and ecological regulations (*7,8*). Process performance was verified in a pilot plant in continuous operation with an average capacity of 10 m^3 per day. This process is based on *in situ* treatment and recycle, so it is not necessary to consider the transport or confine sludges and residual matter. Table 1 shows the average characterization of the streams to be treated in the pilot plant: acidic (stream No. 10), alkaline (stream No. 5), and brine (stream No. 1). This table refers to Figure 1, which shows the schema of treatment processes.

The acidic waste stream was treated to recover Cr(III). The chromium oxide (Cr_2O_3) is the most important chemical compound used to transform hides into leather. The hide becomes an aqueous solution of Cr(III) and is absorbed by tissue. Then, Cr(III) is partially consumed from the aqueous solution to develop coordinate bonds between the functional groups of protein chains. The nitrogen detachment is stopped and hide rotting is avoided. The residual chromium is contained in the acidic effluent (pH 3.5). Cr(III) is recovered by raising the pH and precipitation of its hydroxide in the presence of an organic flocculant (polymer with a medium anionic charge) used to improve the efficiency of the recovery. The chemical reaction carried out in the pilot plant is:

$$Cr_2O_3 + 6\ NaOH = 2\ Cr(OH)_3 + 6\ Na^+ \qquad [1]$$

and the chemical reaction that permits the chromium recovery is:

$$2\ Cr(OH)_3 + 3\ H_2SO_4 = 2\ Cr^{3+} + 3\ SO_4^{=} \qquad [2]$$

The effluents to be treated were generated in two tannery drums located close to the pilot plant, since the volume to be treated

This paper was presented at the Joint United States–Mexico Conference on Fate, Transport, and Interactions of Metals held 14–16 April 1993 in Tucson, Arizona.

The funds to carry out this research were provided by ANACU. The author thanks Oscar Ruiz Carmona for his advice and PUMA for his support.

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Table 1. Measurements for the inlet and outlet streams of the treatment pilot plant.[a]

Stream[b]	Flow, m^3/day	pH	BOD	COD	TSS	TDS	GAF	S(-II)	Cr(III)
1	2.0	8.0	5,000	7,000	10,000	40,000	2,000	–	–
2	2.0	8.0	5,000	7,000	5,000	40,000	2,000	–	–
3	2.0	8.0	4,000	6,500	3,000	40,000	1,500	–	–
4	2.0	7.5	1,500	2,500	150	12,000	10	–	–
5	7.0	12.0	6,000	10,000	8,000	30,000	1,000	4,000	–
6	7.0	12.0	6,000	10,000	6,000	30,000	900	4,000	–
7	7.0	12.0	5,000	8,000	6,000	30,000	500	10	–
8	7.0	7.5	2,500	3,500	250	12,000	10	10	–
9	4.5	7.5	500	300	200	10,000	5	–	–
10	1.0	3.5	2,500	6,000	2,000	20,000	200	–	3,000
11	1.0	3.5	2,500	6,000	2,000	20,000	200	–	3,000
12	0.16	12.0	–	–	–	–	20	–	–
13	0.84	7.5	900	1,800	800	20,000	20	–	1.4
14	0.42	7.2	500	300	200	15,000	5	–	1.4
15	4.5	7.5	500	300	200	10,000	5	–	–
16	0.42	7.2	500	300	200	15,000	5	–	1.4

[a]Parameter units are given in nomenclature. [b]Stream number corresponds to points shown on Figure 1.

was large. These tanning discharges were separately pumped to the pilot plant: The first type was the brine. Others were the alkaline and the acidic wastes. Each effluent was treated by the sequential stages shown in Figure 1. Four classes of treatment were employed in the pilot plant: *a*) a physical separation of suspended solids, *b*) the physical/chemical flocculation-sedimentation of $Cr(OH)_3$, *c*) grease and proteinaceous material, *d*) the catalytic oxidation of sulfides, and *e*) a biological digestion to reduce the BOD. The pollutant parameters of the streams in the pilot plant that were controlled and measured were flow, pH, BOD, COD, Cr(III), GAF, S(–II), TSS, and TDS.

Results

Results of 35 experiments using the pilot plant were essential to determine optimum operating conditions and type of flocculants for the chromium recycling for the local treatment of tannery waste. Theoretical values were not directly applicable because of the presence of surface-active agents and grease in the acidic effluent. Table 1 is a summary of results obtained in the pilot plant. This table shows the segregated flow rates of the streams and the average pollutant concentrations before and after each treatment stage. The statistical significance of the chromium samples was 94.7% for its precipitation and 99.7% for recovery.

After flocculation–sedimentation of $Cr(OH)_3$, it was necessary to provide biological treatment (trickling filter) for the acidic effluent in order to meet BOD stipulated in regulations. The average efficiencies of the treatments is given in Table 2, which were obtained by rating the measurements shown in Table 1. The effluent chromium concentration of 1.4 mg/l was less than the stipulated regulation value (5 mg/l). The efficiency of chromium hydroxide precipitation was 99.5% and chromium extraction from sludge resulted in 99% recovery. Concentrated sulfuric acid was used to obtain a liquor, which was used again in the tanning process. Several hide lots were gradually tanned with recycled water and recovered chromium liquor. The hides tanned until 60% recycled water and using the recovered chromium liquor had an admissible quality in accordance with physical and mechanical standards established internationally. The operating costs of the pilot plant were less than the cost of the water supply (U.S. \$1.10/m^3 vs U.S. \$1.60/m^3). The operating cost includes chemicals and electric power. The cost of recovered chromium is less than the new salt by 75%.

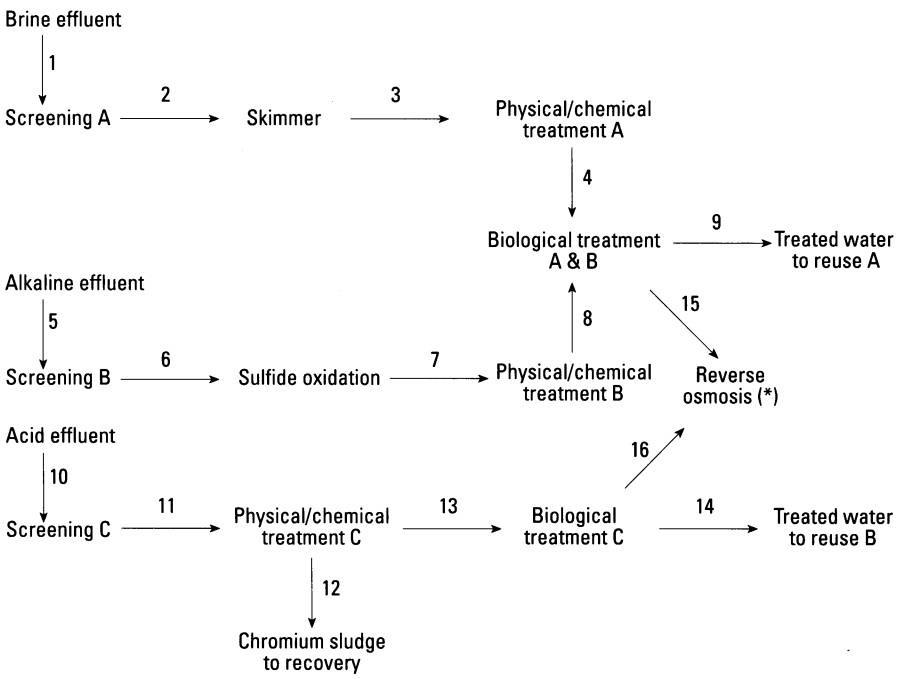

Figure 1. Block diagram of the pilot plant.

Discussion

Flocculation–sedimentation is an appropiate technology for complete chromium removal from tannery wastewater.

With respect to the operating conditions in the pilot plant, the most important variable to be controlled during the chromium removal by PCHT is the pH. Its value determines the quality of treated water and the cost of the treatment. The pH control allows the effective chromium recycling and avoids health risks from chromium exposure. The portion of treated water that is not recycled to tanneries should be passed through an extended

Table 2. Obtained percentage efficiency for treatment stages in the pilot plant.

Treatment stage	Percentage
Chromium precipitation	99.5
Chromium recovery	99.0
PCHT over salty effluent	95.0
PCHT over alkaline effluent	85.0
Sulfide oxidation	90.0
BIOT over salty effluent	65.0
BIOT over alkaline effluent	70.0

aeration system or an activated sludge process to remove BOD. Trickling filters provide rough biological treatment that gives water with industrial quality, but which may not be used for irrigation.

The TDS content in the treated water is high but does not represent a risk to the public health, since these solids are inocuous (NaCl, $SO_4^=$, and $CO_3^=$). Their removal would result in water losses to the atmosphere if solar evaporation were used. Alternatively, the installation of a reverse osmosis system would necessitate a high capital investment and enormous operating costs.

The precipitation–sedimentation of chromium is aviable alternative to evaporation for eliminating heavy metals from rinse and residual waters of metal finishing and printed circuit industries (*9*).

REFERENCES

1. U.S. EPA 440/1-82/016. Development Document for Effluent Limitations Guidelines and Standards for the Leather Tanning and Finishing Point Source Category-Final. Washington:US Environmental Protection Agency, 1982.
2. Industrial Wastewater and Solid Waste Engineering (Cavaseno V and staff of Chemical Engineering, eds). New York:McGraw-Hill, 1980.
3. Glynn W, Baker C, Lore A, Quaglieri A. Mobile Waste Processing System and Treatment Technologies. Park Ridge, NJ:Noyes Data Corp, 1987.
4. Landgrave J. Metodología para el Diseño, instalaci6n y Montaje de Plantas Tratadoras de Efluentes Industriales, International Seminar on Efficient Water Use, Comisi6n Nacional del Agua, 21–25 October, México, D.F., 1991.
5. Ramalho RS. Introduction to Wastewater Treatment Processes, 2nd. ed. San Diego:Academic Press, Inc., 1983.
6. Schroeder ED. Water and Wastewater Treatment. McGraw Hill, 1977.
7 U.S. EPA 440/5-80-035. Ambient Quality Criteria for Chromium, Washington:U.S. EPA, 1980.
8. Diario Oficial de la Federaciòn, México, DF, Jueves 4 de agosto de 1988.
9. Cushnie GC Jr. Electroplating Wastewater Pollution Control Technology. Park Ridge, NJ:Noyes Publications, 1985.